



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: <b>PCT/EP97/07285</b></p> <p>(22) International Filing Date: <b>22 December 1997 (22.12.97)</b></p> <p>(30) Priority Data: <b>08/772,978</b>      <b>23 December 1996 (23.12.96)</b>      <b>US</b></p> <p>(71) Applicant (for all designated States except PL US): <b>SAR-TOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US).</b></p> <p>(71) Applicant (for PL only): <b>CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR).</b></p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): <b>CESKA, Gary, W. [US/US]; 310 Long Ridge, Exton, PA 19341 (US). FAN, Mingxin [CN/US]; 49 Sheffield Lane, West Chester, PA 19380 (US). HORGAN, James [US/US]; 805 Copeland School Road, West Chester, PA 19380 (US).</b></p> <p>(74) Agent: <b>CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, avenue de l'Agent-Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR).</b></p>		<p>(81) Designated States: <b>CA, JP, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b></p> <p><b>Published</b></p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: <b>FREE RADICALLY POLYMERIZABLE SILANE MONOMERS AND OLIGOMERS AND THE METHOD FOR MAKING THEM</b></p> <div style="text-align: center; margin: 20px 0;"> <math display="block">  \begin{array}{c}  \text{O} \qquad \qquad \text{O} \\  \parallel \qquad \qquad \parallel \\  (\text{CH}_2=\text{C}-\text{C}-\text{X})_n-\text{A}-\text{X}-\text{C}-\text{CH}-\text{CH}_2-\text{N}-\text{R}^3-\text{SiY}^1\text{Y}^2\text{Y}^3 \\    \qquad \qquad \qquad   \qquad \qquad   \\  \text{R}^1 \qquad \qquad \qquad \text{R}^1 \qquad \qquad \text{R}^2  \end{array}  \quad (I)  </math> </div> <div style="display: flex; justify-content: space-around; margin-top: 20px;"> <div style="text-align: center;"> <math display="block">  \begin{array}{c}  \text{O} \\  \parallel \\  (\text{CH}_2=\text{C}-\text{C}-\text{X})_{n+1}-\text{A} \\    \\  \text{R}^1  \end{array}  \quad (II)  </math> </div> <div style="text-align: center;"> <math display="block">  \begin{array}{c}  \text{H}-\text{N}-\text{R}^3-\text{SiY}^1\text{Y}^2\text{Y}^3 \\    \\  \text{R}^2  \end{array}  \quad (III)  </math> </div> </div> <p>(57) Abstract</p> <p>Compounds of formula (I), wherein R<sup>1</sup> is H or CH<sub>3</sub>; n is 1 to 6; A is a bivalent to heptavalent linking group; X is O, S, NH; R<sup>2</sup> is H or a C<sub>1</sub>-C<sub>20</sub> organic group; R<sup>3</sup> is a divalent linking group; and each of Y<sup>1</sup>Y<sup>2</sup>Y<sup>3</sup>, which may be the same or different, represents alkoxy, carboxy, alkoxy ether, alkyl, aryl. A process of making compounds of formula (I) comprises reacting a multifunctional (meth)acrylate of formula (II), with a silane of formula (III). Compounds (I) are shown to be useful as coupling agents or adhesion promoters in free radically, radiation curable compositions where the odor of allyl methacrylate is undesirable. The associated methods, curable compositions, coatings, adhesives and coated articles are also disclosed.</p>		

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FREE RADICALLY POLYMERIZABLE SILANE MONOMERS AND OLIGOMERS AND  
THE METHOD FOR MAKING THEM.

This invention relates to monomers and oligomers which contain both (meth)acrylate and silane functional groups, the use of such monomers and oligomers as adhesion promoting coupling agents in free radically curable compositions, and radiation curable compositions containing such monomers and oligomers.

It has long been known that organic coatings on inorganic substrates such as glass and metal lose adhesion upon exposure to moisture. To avoid damage to the coatings and provide stable adhesion to the substrates, various coupling agents or adhesion promoters are generally incorporated into the coating compositions. Silane coupling agents have been widely used to enhance the adhesion between substrate coatings. Most silane coupling agents are designed for two part systems other than one component UV curable systems. For example, US Patent 4,849,462 describes a coating composition comprising a UV curable polyurethane polyacrylate containing about 0.5 to 5.0% mercapto polyalkoxysilane.

US Patent 5,146,531 describes an inner primary coating that contains an acrylated urethane oligomer based on a hydrocarbon polyol, reactive diluents, an organofunctional adhesion promotor, and a photoinitiator.

In the past 20 years, radiation curing has become more and more popular since it provides low or zero volume emission and high productivity. Radiation cure technology has been widely used in coatings, inks and adhesives. Radiation curable compositions are typically mixtures of monomers, oligomers, photoinitiators, or additives which are applied to the substrates and cured in place via ultraviolet light. Silane coupling agents have been widely used to improve adhesion in traditional coatings and composites based on epoxy chemistry. However, the application and selection of silane agents depends on cure mechanisms. In the radiation curable case, only one compound, gamma-methacryloxypropyl

trimethoxysilane, is compatible with the cure mechanism and available.

Gamma-methacryloxypropyl trimethoxysilane monomer is a well known commercially available coupling agent for bonding coatings to substrates. The coupling agent is mixed with other copolymerizable monomers such (meth)acrylates, i.e., acrylates, methacrylates, or mixtures thereof, and the mixture of monomers is applied to a surface and cured. This methacryloxypropyl trimethoxysilane coupling agent of the prior art is prepared from allylmethacrylate, a volatile and odorous compound. The presence of the allylmethacrylate starting material along with the methacryloxypropyl trimethoxysilane monomer coupling agent also causes odor problems with the cured coatings. Other silane-based coupling agents are available, but are mainly directed to two-part, non-(meth)acrylate systems. See Waldman, Silane Coupling Agents Improve Performance, Modern Paints and Coatings, Feb. 1996.

PCT publication WO 96/12749 of 2 May 1996 shows silane oligomers and radiation curable coating compositions for optical fiber coating. The silane oligomers are high in molecular weight (500-11,000) and a high level of silane oligomer is needed, typically about 5-99% of the coating composition. These silane oligomers are typically prepared based on urethane chemistry and urethane linkage.

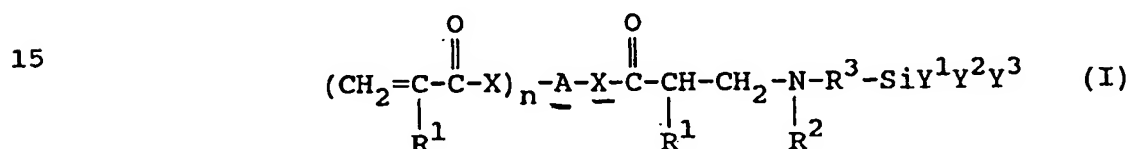
Derwent abstract 95-225640/30 relating to DE-4 416 857 of 29 June 1995 shows hydrolyzable and polymerizable silane(s) useful in coating, adhesive, and molding compositions and composites prepared from reactive silane and unsaturated compound and polycondensed to hetero polysilicic acid compound or polymerized. These silanes, which have carboxylic acid functional groups for use in the radiation-hardenable binders, are prepared from hydroxy containing compounds and acid anhydride containing silanes.

It is an object of this invention to provide free radically polymerizable silane coupling agents which are especially useful in the radiation curing and peroxide curing

formulations, but do not suffer from the disadvantages of prior art coupling agents such as gamma-methacryloxypropyl trimethoxysilane.

It is another object of this invention to provide the method for preparation of the new silane containing (meth)acrylates.

A further object of this invention is to provide improved UV curable compositions with good adhesions to substrates. These objects and others as will become apparent from the following disclosure, are achieved by the present invention which comprises in one aspect compounds of the formula (I) :



wherein :

- $R^1$  is H or  $CH_3$  ;
- $n$  is 1 to 6
- $A$  is a bivalent to heptavalent linking group ;
- $X$  is O, S, NH ;
- $R^2$  is H or a  $C_1-C_{20}$  organic group ;
- $R^3$  is a divalent linking group ; and
- each of  $Y^1Y^2Y^3$ , which may be the same or different, represents alkoxy, carboxy, alkoxy ether, alkyl, aryl.

Preferred compounds of formula (I) are those

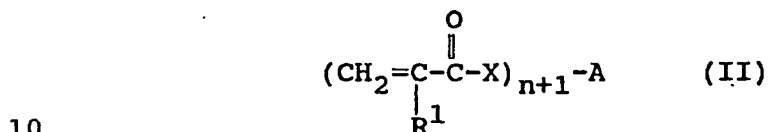
wherein :

- $X = O$  ;
- $A$  is urethane, polyether, polyester, alkylene, aromatic, alkoxyalkylene, alkoxyalkyl aromatic ;
- $R^2$  is H or  $-CH_2-CH(R^4)-C(=O)-R^5$ ,

wherein  $R^4$  is H or  $CH_3$  and  $R^5$  is an organic group or a group resulting from the post-reaction of a compound (I) having  $R^2 = H$ , with an NH- reacting compound such as an epoxyde or an isocyanate or a mono-unsaturated monomer ;

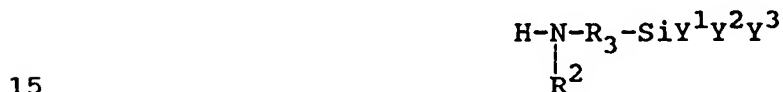
- R<sup>3</sup> is a divalent organic group having 1 to 6 carbon atoms;
- Y<sup>1</sup>, Y<sup>2</sup> and Y<sup>3</sup> are methoxy or ethoxy.

In another aspect, the invention comprises a method of making such compounds of formula (I) comprising  
 5 reacting a multifunctional (meth)acrylate of formula (II) :



10

wherein R<sup>1</sup>, X, n and A are as defined above,  
 with a silane of formula (III) :

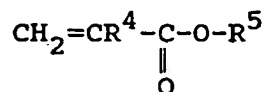


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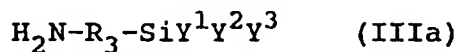
wherein R<sup>2</sup>, R<sup>3</sup>, Y<sup>1</sup>, Y<sup>2</sup> and Y<sup>3</sup> are as defined above.

When R<sup>2</sup> is  $-\text{CH}_2-\text{CHR}^4-\text{C}(=\text{O})-\text{O}-\text{R}^5$ , the process

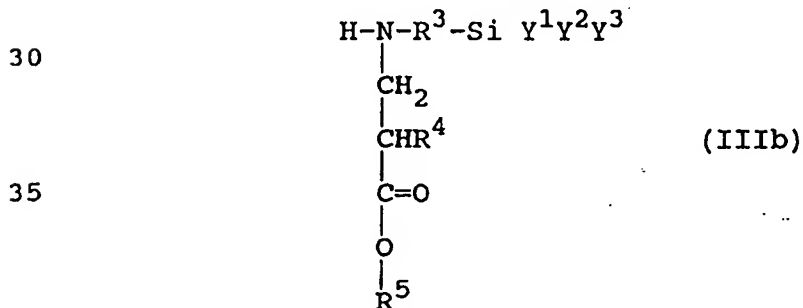
20 according to the present invention comprises the preliminary  
 step of reacting a compound of formula (IV) :



25 wherein R<sup>4</sup> and R<sup>5</sup> are as defined above,  
 with a compound of formula (IIIa) :



in order to obtain the compound of formula (IIIb) :



30

35

which is then reacted with a compound of formula (II) as defined above.

According to an embodiment of the present process, leading to a compound of formula (I) wherein  $R^2$  is different from H, said process further comprises the post-reaction of  
5 a compound of formula (I) wherein  $R^2 = H$  with an NH-reacting compound such as an epoxyde or an isocyanate or a mono-unsaturated monomer.

The silane monomers and oligomers of the invention  
10 are useful as coupling agents in radiation curable coatings, adhesives, and other resins, wherever the gamma-methacryloxypropyl trimethoxysilane coupling agents of the prior art had been used, and especially in applications where the odor of allylmethacrylate is undesirable. The radiation  
15 can be UV or electron beam, with or without photoinitiator present.

The coating composition preferably comprises :

- (1) 0.1 to 50% silane monomers or oligomers of formula (I); ✓
- (2) 0 to 80% by weight of (meth)acrylate oligomers ;
- 20 (3) 1 to 50% by weight of (meth)acrylate monomers ; ✓ and
- (4) 0.1 to 30% by weight of additives. ✓

The compounds of formula (I) can be prepared by reaction of (1) di(meth)acrylates or multifunctional (meth)acrylates of formula (II) and (2) aminoalkylsilanes of  
25 formula (III). The reaction is typically exothermic and no catalyst is needed.

The preparation of the silane containing monomers and oligomers can be performed simply by reacting the silane compound of formula (III) with monomers of formula (II) with  
30 or without catalyst present. Preferably, the reaction is carried out at temperature range from 0° to 150°C. Preferably, the reaction temperature is about 0 to 100°C. Most preferably, the reaction temperature is in the range of 20 to 80°C. The silane monomers of formula (I) can also be  
35 prepared *in situ* in the radiation curable composition.

The stoichiometric balance between amino functionality and acrylate functionality is in the range of 1:0.1 to 1:50, preferably, the range is 1:0.5 to 1:10, and more preferably in the range of 1:0.5 to 1:5. After the  
5 reaction, the silane compound of formula (III) is attached to monomers of formula (II), and a new bifunctional material is formed. The new bifunctional silane monomers may be further modified with epoxides and (meth)acrylates.

Examples of the silanes of formula (III) are  
10 aminopropyltrimethoxysilane, aminopropyltriethoxysilane, aminoalkyltrimethoxysilane, aminoalkyltriethoxysilane, aminobutyltrimethoxysilane, aminobutyltriethoxysilane, aminopentyltrimethoxysilane, aminopentyltriethoxysilane.

In formula (II), A can be urethane, polyether,  
15 polyester, alkylene, aromatic, alkoxyated alkylene, alkoxyated aromatic, and the like. Suitable compounds of formula (II) include di and multifunctional (meth)acrylates such as 1,6-hexanediol diacrylate, 1,4-butanediol diacrylate, polyethyleneglycol or polypropyleneglycol diacrylate, 1,6-  
20 hexanediol dimethacrylate, trimethylolpropane triacrylate, epoxy acrylaturethaneane acrylate, polyester diacrylate, and the like. The (meth)acrylate monomers or oligomers of formula (II) may be used in neat form or a mixture of several monomers and/or oligomers. Difunctional acrylate oligomers  
25 are preferred such as polyester diacrylates, polyether diacrylate, difunctional acrylate urethane oligomers. Urethane diacrylates based on polyether or polyolefin oligomer diols are preferred. (Meth)acrylates are used as reactive diluents, and may have one or more acrylate functionality.  
30 Examples are hexylacrylate, 2-ethylhexylacrylate, isobornylacrylate, decyl-acrylate, laurylacrylate, stearylacrylate, ethoxyethoxyethyl-acrylate, isodecylacrylate, isooctylacrylate, ethyleneglycol-phenyletheracrylate, polyethyleneglycolphenyletheracrylate,  
35 polypropyleneglycolphenylether acrylate, polyethyleneglycol nonylphenyletheracrylate, 1,6-hexanedioldiacrylate, trimethylolpropanetriacrylate, triethyleneglycol diacrylate,

pentaerythritoltriacylate, ethoxylated bisphenol-A diacylate, tripropyleneglycol diacylate, and the like. Y can be an alkoxy, carboxy, alkoxyether, alkyl, aryl group, and the three groups can be the same or different. Preferably, all Y groups are the same, and are low molecular weight groups having less than 8 carbon atoms, more preferably less than 4 carbon atoms. Preferred examples of Y groups are methoxy, ethoxy, acetoxy, and methoxyethoxy.

The silane compound of formula (III) contains one non hydrolyzable amino functional group and at least one hydrolyzable group. The amino functional group reacts with A of the compound of formula (II) to form chemical linkage.

Furthermore, the reaction according to the present invention can be made advantageously in the presence of a polymerization inhibitor, such as 4-methoxyphenol.

The invention further relates to radiation curable compositions where adhesion to a substrate is desirable, such as coating and adhesive compositions, comprising an effective amount of the silane monomer and oligomer compounds of formula (I).

The radiation curable compositions can be prepared by combining the silane compounds of formula (I) with other (meth)acrylate monomers and oligomers, and with other compounds or additives, to form radiation curable compositions. Other optional additives are light sensitive and light absorbing materials, catalysts, initiators, lubricants, wetting agents, organofunctional silane or silicones, antioxidants, and stabilizers. Photoinitiators are optional, but compositions suitable for electron beam cure do not typically require photoinitiators.

A photoinitiator is usually required for a UV curable composition, photoinitiators can be eliminated for an electron beam curable composition. The photoinitiator, when used in the composition to initiate radiation cure, provides reasonable cure speed without causing premature gelling of the composition. Examples of free radical photoinitiators are hydroxycyclohexylphenyl ketone, hydroxymethyl phenylpropanone,

dimethoxyphenylacetophenone, 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropanone-1, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-(2-hydroxyethoxy)phenyl-2(2-hydroxy-2-propyl)-ketone, diethoxyphenyl acetophenone, 2,4,6-trimethylbenzoyl diphenylphosphine.

Another embodiment of the invention is a method of promoting adhesion or coupling of a radiation curable composition to a substrate comprising adding a compound of  
10 formula (I) to the radiation curable composition and thereafter exposing the composition to radiation. Another embodiment of the invention concerns articles obtained from radiation curable composition comprising a coupling agent of formula (I) and at least one unsaturated monomer and having  
15 adhesion properties to a substrate. The present invention also encompasses an article comprising a substrate coated with a composition as defined above in the cured state.

Substrates such as glass can be used.

The following examples present a few embodiments  
20 of the invention.

#### EXAMPLE 1

In a reactor, 75 grams of hexanediol diacrylate, 0.12 gram of 4-methoxyphenol, and 50 grams of aminopropyltriethoxysilane were added, and the mixture was  
25 stirred at room temperature for 4 hours and became a viscous liquid. The addition reaction was exothermic. As the aminopropyltriethoxysilane was consumed, the acrylated silane monomer was formed.

#### EXAMPLE 2

30 In a reactor, 60 grams of hexanediol diacrylate, 0.20 gram of 4-methoxyphenol, and 40 grams of aminopropyltrimethoxysilane were added and the mixture was stirred at room temperature for 4 hours. As

aminopropyltriethoxysilane was consumed, the acrylated silane monomer was formed.

#### EXAMPLE 3

50.0 grams of product from Example 1 and 17.3 grams  
5 of n-butylglycidyl ether were mixed at room temperature. The final mixture has much better stability.

#### EXAMPLE 4

94.0 grams of ethoxyethoxyethylacrylate and 90.0  
grams of aminopropyltrimethoxysilane were reacted at room  
10 temperature. The mixture became warm as heat was generated from the reaction. The reaction was kept at room temperature for 20 hours.

To the resultant monomer product, 0.10 gram of 4-methoxyphenol and 113 grams of hexanediol diacrylate were  
15 added. The reaction mixture was kept at 80°C for 24 hours. Analysis by gas chromatograph showed no residual aminopropyltrimethoxysilane present.

#### EXAMPLE 5

Tetrahydrofurfuryl acrylate (78.0 g) and  
20 aminopropyltrimethoxy silane (90.0 g) were stirred at room temperature and heat generation was noticed. The reaction completed overnight. No residual aminotrimethoxysilane was detected by gas chromatograph.

To the resultant product, 1,4-butanediol diacrylate  
25 (100.0 g) was added and the reaction mixture was reacted at 80°C for 16 hours to form an oligomer.

#### EXAMPLE 6

A UV curable composition was prepared using 57.0  
g of urethane acrylate oligomer (CN 964 E75 grade from

E-6

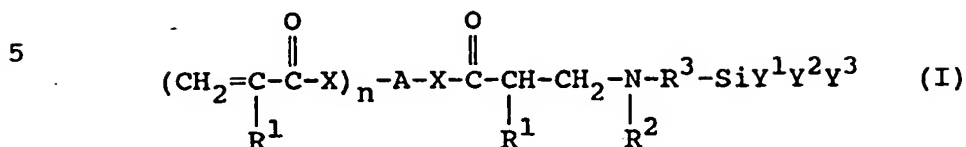
Sartomer Company), 33.25 g of 2-phenoxyethylacrylate (SR 339 grade from Sartomer Company), 4.75 g of oligomeric photoinitiator (KIP 100F grade from Sartomer Company), and 5.0 g of silane monomer from Example 4. The formulation was  
5 applied to an aluminum panel and cured using two 157,5 watt/cm (400 watt/inch) Fusion H lamps at 15.2 m/min (50 fpm) speed with two passes. The film was fully cured with a tack free surface.

The cured aluminum panel was placed in a 60°C oven  
10 for 10 min followed by crosshatch adhesion test which showed 100% retention. A control formulation identical to the above formulation without the silane monomer showed 0% retention under the same conditions.

While the invention has been described in detail  
15 herein, various alternative embodiments and improvements should become apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth in the following claims.

CLAIMS

1 - Compound of the formula (I) :



wherein :

- 10 -  $\text{R}^1$  is H or  $\text{CH}_3$  ;
- n is 1 to 6
- A is a bivalent to heptavalent linking group ;
- X is O, S, NH ;
- $\text{R}^2$  is H or a  $\text{C}_1$ - $\text{C}_{20}$  organic group ;
- 15 -  $\text{R}^3$  is a divalent linking group ; and
- each of  $\text{Y}^1\text{Y}^2\text{Y}^3$ , which may be the same or different, represents alkoxy, carboxy, alkoxy ether, alkyl, aryl.

2 - Compounds according to claim 1, characterized by the fact that  $\text{X} = \text{O}$ .

- 20 3 - Compounds according to anyone of claims 1 and 2, characterized by the fact that A is urethane, polyether, polyester, alkylene, aromatic, alkoxyated alkylene, alkoxyated aromatic.

4 - Compounds according to anyone of claims 1 to 25 3, characterized by the fact that  $\text{R}^2$  is H or  $-\text{CH}_2-\text{CHR}^4-\text{C}-\text{O}-\text{R}^5$ ,  
 $\parallel$   
 $\text{O}$

wherein  $\text{R}^4$  is H or  $\text{CH}_3$  and  $\text{R}^5$  is an organic group or a group resulting from the post-reaction of a compound (I) wherein  
 30  $\text{R}^2 = \text{H}$  with an NH-reacting compound such as an epoxyde or an isocyanate or a mono-unsaturated monomer.

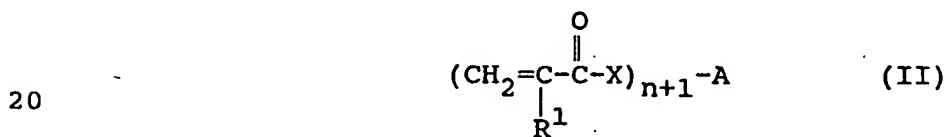
5 - Compounds according to anyone of claims 1 to 4, characterized by the fact that  $\text{R}^3$  is a divalent organic group having 1 to 6 carbon atoms.

- 35 6 - Compounds according to anyone of claims 1 to 5, characterized by the fact that  $\text{Y}^1$ ,  $\text{Y}^2$  and  $\text{Y}^3$  are methoxy or ethoxy.

7 - Compounds according to claim 1, characterized by the fact that it is :

- a reaction product of hexanediol diacylate with aminopropyltriéthoxysilane ;
- 5 - a reaction product of hexanediol diacrylate with aminopropyltriméthoxysilane ;
- a reaction product of hexanediol diacrylate with the reaction product of ethoxyethoxyethyl acrylate and aminopropyltrimethoxysilane ; or
- 10 - a reaction product of 1,4-butanediol diacrylate with the reaction product of tetrahydrofurfuryl acrylate and aminopropyl trimethoxysilane.

8 - A process of making compounds of formula (I) as defined in anyone of claims 1 to 7, characterized by the  
15 fact that it comprises reacting a multifunctional (meth)acrylate of formula (II) :



wherein  $\text{R}^1$ , X, n and A are as defined in claim 1, with a silane of formula (III) :



wherein  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{Y}^1$ ,  $\text{Y}^2$  and  $\text{Y}^3$  are as defined in claim 1.

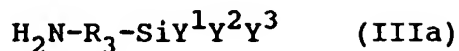
9 - A process according to claim 8 for making  
30 compounds of formula (I) wherein  $\text{R}^2$  is  $-\text{CH}_2-\text{CHR}^4-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{O}-\text{R}^5$ ,

wherein  $\text{R}^4$  and  $\text{R}^5$  are as defined in claim 4, characterized by the fact that it comprises the preliminary step of reacting a compound of formula (IV) :

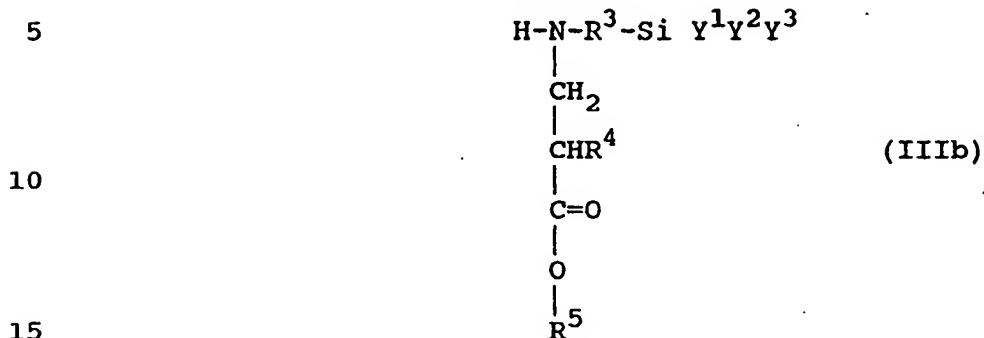


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wherein  $R^4$  and  $R^5$  are as defined above,  
with a compound of formula (IIIa) :



in order to obtain the compound of formula (IIIb) :



which is then reacted with a compound of formula (II).

10 - A process according to claim 8 leading to a compound of formula (I) wherein  $R^2$  is different from H, characterized by the fact that it further comprises the post-  
20 reaction of a compound of formula (I) wherein  $R^2 = H$  with an NH-reacting compound such as an epoxyde or an isocyanate or a mono-unsaturated monomer.

11 - Use of a compound as defined in anyone of claim 1 to 7 or prepared by a process as defined in anyone of  
25 claim 8 to 10 as an adhesion promoting agent or as a coupling agent.

12 - Method of promoting adhesion or coupling of a radiation curable composition to a substrate comprising adding a compound as defined in anyone of claims 1 to 7 or  
30 prepared by a process as defined in anyone of claims 8 to 10 to the radiation curable composition and thereafter exposing the composition to radiation.

13 - Radiation curable composition comprising a coupling agent compound as defined in anyone of claims 1 to  
35 7 or obtained by a process as defined in anyone of claims 8 to 10 and one or more unsaturated monomers, the composition having adhesion properties to a substrate.

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14 - Article comprising a substrate coated with a composition as defined in claim 13 in the cured state.

15 - Article according to claim 14, wherein the substrate is glass.

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# INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/EP 97/07285

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F7/18 C07F7/08 C08L75/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 298 734 A (SHIN-ETSU CHEMICAL CO., LTD) 11 January 1989 see the whole document ---	1-10
A	DE 40 11 044 A (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG EV) 10 October 1991 see the whole document ---	1-10
A	WO 96 12749 A (DSM NV) 2 May 1996 cited in the application see the whole document ---	1-15
A	DE 44 16 857 A (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG EV) 29 June 1995 cited in the application see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search

9 April 1998

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# INTERNATIONAL SEARCH REPORT

information on patent family members

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